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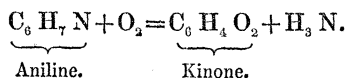
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IV. "Note on Kinone." By A. W. HOFMANN, LL.D., F.R.S.

Received June 23, 1863.

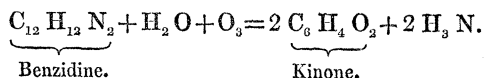
The easy and perfect transformation of beta-phenylene-diamine into kinone, which I have pointed out in a former communication, has induced me to examine the action of oxidizing agents upon other derivatives of the phenyl-series.

Aniline, when submitted to the action of a mixture of peroxide of manganese and sulphuric acid, furnishes very appreciable quantities of kinone, which sublimes, the residue containing the sulphates of ammonium and manganese.



This equation represents, however, only one phase of the reaction. The result, in a measure, depends upon the mode of experimenting: one part of aniline, four parts of peroxide of manganese, and four parts of sulphuric acid diluted with its own bulk of water were found to be appropriate proportions. But the amount of kinone is always limited, the greater portion of the aniline undergoing further alterations.

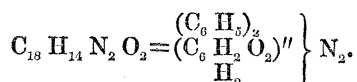
The experiment succeeds much better with *benzidine*. On heating the mixture of this base with the oxidizing agents, torrents of kinone are instantaneously evolved, which condense in the receiver into magnificent yellow needles. The quantity of kinone thus obtained corresponds to the amount of benzidine employed.



The transformation of aniline into kinone, very naturally suggested the idea of examining the behaviour of these two bodies with one another.

The reddish-brown liquid obtained by dissolving kinone in aniline very rapidly solidifies into a crystalline mass. The crystalline product of the reaction proved to be insoluble in water, alcohol, and ether, and several solvents which I tried, so that purification by crystallization became impossible; it was therefore found to be convenient to accomplish the reaction in the presence of a large quantity of boiling alcohol. The brown liquid deposits on cooling reddish brown almost metal-lustrous scales, which by washing with cold alcohol become perfectly pure.

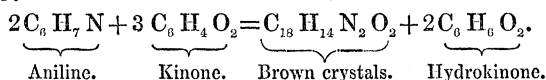
The analysis of this substance shows that it has the following composition:—



The complementary product of the reaction was discovered without difficulty in the mother-liquor of the reddish-brown crystals. The saline

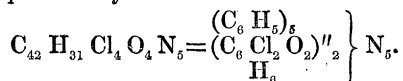
residue which is left on evaporating this liquid with hydrochloric acid, is a mixture of hydrochlorate of aniline and *hydrokinone*. They are easily separated by treatment with ether, which dissolves the hydrokinone, leaving the aniline-salt as an insoluble residue. The ethereal solution, when evaporated, yields colourless needles of hydrokinone possessing all the characteristic properties which distinguish this remarkable body. Addition of ferric chloride to their aqueous solution produces at once the green prisms, with golden lustre of the intermediate hydrokinone.

The action of kinone upon aniline is therefore represented by the following equation:—

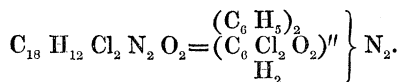


The study of this reaction has induced me to repeat an experiment mentioned by M. Hesse in his beautiful researches on the kinone group*.

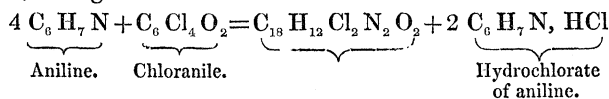
By submitting aniline to the action of *chloranile* (tetrachlorokinone), M. Hesse has obtained a compound crystallizing in reddish-brown scales, the general properties of which resemble those of the kinone derivative above described. The composition of the compound formed with chloranile M. Hesse represents by the formula



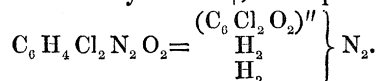
I cannot confirm this somewhat complicated expression. In studying the action of chloranile upon aniline, I have observed all the phenomena described by M. Hesse: the compound formed had all the properties which he assigns to it, but was found on analysis to contain about 2 per cent. of carbon less than he had observed. The substance examined by me contained



This is the formula of the kinone derivative with two atoms of hydrogen replaced by chlorine. The action of chloranile on aniline is therefore, in a measure, analogous to that of kinone.



The formula which I propose to substitute for that of M. Hesse is moreover supported by the result obtained in studying the deportment of chloranile under the influence of ammonia. This gives rise to the formation of *chloranilamide* discovered by Laurent†, and represented by the formula



* Ann. Chem. Pharm. cxiv. p. 307.

† Laurent, xix. 323.

I have ascertained that toluidine furnishes, both with kinone and chloranile, analogous compounds. The higher percentage of carbon observed by M. Hesse may possibly find a satisfactory explanation in the contamination with toluidine of the aniline which has served for his experiments. Commercial aniline invariably contains more or less toluidine.

V. "Researches on Colouring Matters derived from Coal-tar.—
I. On *Aniline-yellow*." By A. W. HOFMANN, LL.D., F.R.S.
Received June 29, 1863.

In a short paper submitted to the Royal Society in the commencement of last year, I have described a few experiments on the remarkable new colouring matters derived from aniline, which of late have attracted such general attention. This paper had more particularly reference to aniline-crimson, the industrial production of which, in the hands of Mr. E. Nicholson, has reached so high a degree of perfection that the analysis of this compound and of its numerous salts presented no serious difficulty. But the problem was not solved by establishing the formula of rosaniline and its salts: by far the more important obstacles remained to be conquered; the molecular constitution of rosaniline, on which at that time I had not even been able to offer an hypothesis, and the genesis of this well-defined triamine from aniline, had still to be traced. Since that time considerable progress has been made towards the solution of this problem. Some of the latest observations which I have had the honour of submitting to the Royal Society will doubtless help to untie this knot. Nevertheless many doubtful points still remain to be cleared up, and I found it desirable for the better elucidation of the subject to investigate simultaneously several of the other artificial organic colouring matters, in order to trace if possible analogies of composition and constitution in these substances, which, it was reasonable to hope, would throw some light upon the principal subject of the inquiry.

The present moment appeared to be particularly appropriate for an investigation of this kind. The International Exhibition has brought together a collection of these new bodies, such as no other occasion could possibly have assembled in one place and at one time, displaying in a remarkable manner the rapidity with which the industry of our time assimilates and, in many cases, anticipates the results of pure science.

I have commenced the study of a few of the new colouring matters which several of the distinguished exhibitors of these compounds have placed at my disposal—a study which has been greatly facilitated by the zeal and experimental skill of a young chemist, Dr. A. Geyger, who has assisted me in these experiments. Owing to the number of these substances, and in some cases the difficulties of the reactions to be disentangled, some time must elapse before their investigation can be finished,